

Homogeneous Electron Exchange in Catalytic Polarographic Reduction

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Electron transfer reactions between an electrolytically generated anion radical $A^{\cdot-}$ and a more difficultly reducible compound (BX) forming an unstable anion radical has been studied by means of classical polarography. The rate of the reduction of BX by $A^{\cdot-}$, measured by the catalytic increase of the wave-height of A, is dependent on the difference in the reduction potentials of A and BX; the electron transfer reaction or the decomposition of $BX^{\cdot-}$ may be rate determining. Comparison of results from direct and indirect electrolytic reduction may throw light on the influence of the electrode on product distribution.

Polarographic “catalytic currents” are well-known (Fig. 1), especially in inorganic polarog-

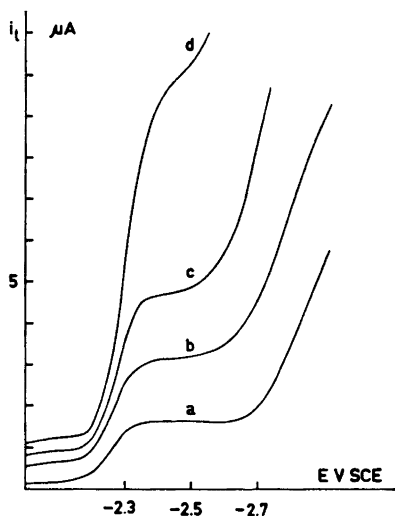
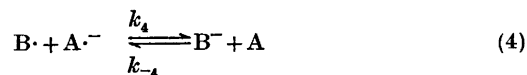
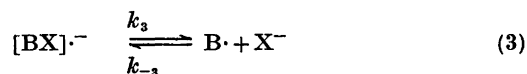
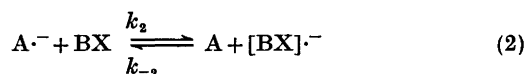
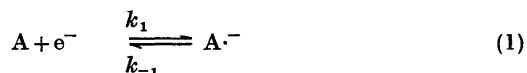
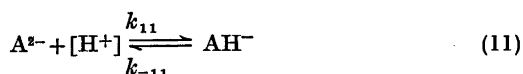
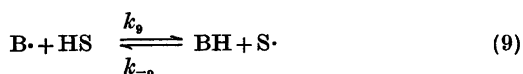
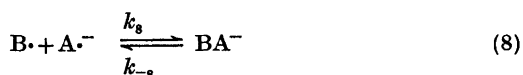
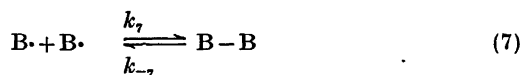
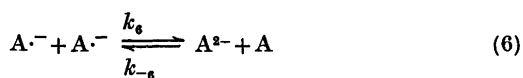


Fig. 1. Polarograms of chrysene (4×10^{-4} m) in DMF containing tetrabutylammonium iodide and (a) O; (b) 5×10^{-4} m; (c) 1.5×10^{-3} m; (d) 4×10^{-3} m bromobenzene.

raphy, *e.g.* the hydrogen peroxide¹ or hydroxylamine² reoxidation of ferrous ions during the polarographic reduction of ferric ions, or the reoxidation of Ti^{3+} by hydroxylamine³ during polarography of Ti^{4+} . A theory⁴⁻⁶ for the connection between the ratio of the limiting current to the diffusion controlled current and the rate constant of the catalyzing reaction has been developed.

A similar increase of a polarographic current due to a regeneration of the depolarisator by electron exchange with another species seems not to have been investigated in detail for organic molecules.⁷ The phenomenon seems, however, to be rather general provided certain requirements are met, and below is given a preliminary report on a number of such cases including examples of many different types of compounds. All the examples can be fitted into the general scheme





Scheme 1.

In this scheme A gives a polarographic wave at a less negative potential than that of BX; the radical anion $A^{\cdot-}$ produced in (1) should be stable measured on the time scale relevant here. The reoxidation of $A^{\cdot-}$ to A by BX (2) or by B^{\cdot} (4) gives rise to the observed catalytic current.

BX is a molecule, the anion radical of which is cleaved into the neutral radical B^{\cdot} and the stable ion $X^-(3)$. The radical B^{\cdot} will in most cases, but not all, exchange an electron with $A^{\cdot-}$ (4), undergo dimerization (7), coupling (8), hydrogen abstraction (9), or direct reduction at the electrode (10) may occur. Usually (2) and (4) together result in the reoxidation of two $A^{\cdot-}$ for every BX reduced to BH and X^- . It may be noted, that the reoxidation of Fe^{2+} by hydrogen peroxide and hydroxylamine also fits into the scheme with these compounds acting as BX compounds where the first electron uptake is followed by a rapid cleavage to a neutral radical and a stable anion.

As A-compounds have been employed aromatic hydrocarbons, heterocyclic compounds, aromatic ketones, esters, nitriles, and nitro compounds, but other types may work as well. As BX-compounds have been used alcohols, esters, halides, sulphonamides, and azides.

In Table 1 are presented some of the results. In column 1 and 2 are the A and BX compounds, respectively; in the third column is given the difference ΔE between the half-wave potentials of A and BX, and in the fourth one the rate constant k calculated according to the

Table 1. Rate constants of the reaction responsible for the "catalytic" increase in limiting current of a number of aromatic systems (A) in the presence of compounds (BX), which form unstable anion radicals.

A	BX	ΔE V	k
Biphenyl	Chlorobenzene	0.27	2.3×10^4
1-Methylnaphthalene	»	0.28	1.2×10^4
Naphthalene	»	0.32	5×10^3
2-Methylphenanthrene	»	0.37	1.6×10^3
Phenanthrene	»	0.39	1.2×10^3
Terphenyl	»	0.52	1.7×10^1
Benzonitrile	»	0.55	8
Chrysene	Bromobenzene	0.36	4×10^3
Methyl benzoate	»	0.39	1.3×10^3
Biphenyl	Fluorobenzene	0.32	9×10^1
Chinoxaline	1-Bromonaphthalene	0.39	1.5×10^1
Acridine	»	0.45	5
Chinoxaline	9-Bromophenanthrene	0.32	2.7×10^1
Benzophenone	D,L-Stilbene dichloride	0.30	3×10^3
»	meso-Stilbene dichloride	0.28	9×10^3
Chrysene	2-Naphthyldimethylcarbinol	0.33	3.3×10^3
Pyrene	N,N-Dimethyl-p-toluenesulphonamide	0.33	4×10^3
Anthracene	Ethyl p-toluenesulphonate	0.23	4×10^3
Benzocinnoline	Phenyl azide	0.28	5×10^3
2-Nitroanisole	»	0.48	5×10^1

Koutecký equation.⁶

The results given in Table 1 will be discussed qualitatively on the basis of Scheme 1. The Koutecký equation gives a formal rate constant which could include many of the rate constants in the scheme, but the more significant ones would most likely be k_2 or k_3 or both.

If the most significant factor in k is k_2 , and thus (3) and (4) very fast, k would, for a given BX, depend on the potential difference between E°_A and E°_{BX} , the rates of the equilibria $A + A^{\cdot-} \rightleftharpoons A^{\cdot-} + A$ (12), and the corresponding one for $BX/BX^{\cdot-}$ (13). The rate constants for a number of equilibria of the type (12) have been measured from the broadening of the lines in the EPR spectra⁸⁻¹² and are generally¹² between 10^7 and 10^9 M⁻¹ s⁻¹. The instability of the $BX^{\cdot-}$ makes it difficult to obtain data for (13), but it seems reasonable to assume, that the rate of electron exchange for aromatic BX compounds (13) is of the same magnitude as that of (12). The reported rate constant for (12) includes nitrobenzene⁸ (3×10^7 M⁻¹ s⁻¹) and benzonitrile⁹ (2×10^8 M⁻¹ s⁻¹), with benzene,¹⁰ naphthalene,¹¹ and benzophenone¹² having rate constants between these limits. In this connection the results from the pulse radiolysis on the rate of electron transfer reactions in solution are of interest.¹⁴⁻¹⁶

From the equation¹⁷ $k_{ABX} = (k_A k_{BX} K_{ABX} f)^{1/2}$, where k_{ABX} , k_A , and k_{BX} are the rate constants of (2), (12), and (13), respectively, K the equilibrium constant of (2), and f a factor which often is close to 1, the dependence of k_{ABX} on ΔE° can be estimated. The data for k_A ⁸⁻¹² show only a moderate variation, and regarding k_A as constant is probably not more than a factor 5 off. This approximation would make it possible to predict a decrease in the observed rate constant (2) with a factor 10 for a given BX for an increase in ΔE° by 0.12 V.

In Fig. 2 is shown as ordinate the logarithm of rate constants k for several A, calculated from Koutecký equation,⁵ in the presence of chlorobenzene as the BX-compound, and ΔE as abscissa. Instead of ΔE° is taken the difference in polarographic half-wave potential between that of A and that of chlorobenzene, as the reversible redox potential for chlorobenzene is difficult to obtain due to the instability of its anion radical. Extrapolation of the experimental values to $\Delta E = 0$ suggests $k \sim 5 \times 10^7$; the value,

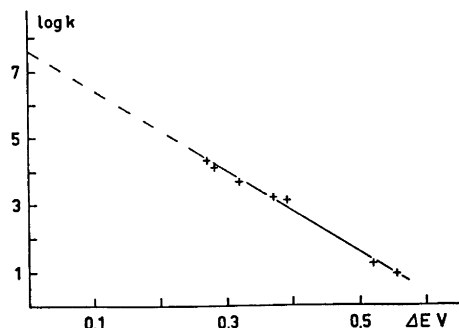


Fig. 2. Dependence on ΔE of the logarithm of the rate constants⁵ of the chlorobenzene reoxidation of the following anion radicals (with increasing ΔE): biphenyl, 1-methylnaphthalene, naphthalene, 2-methylphenanthrene, phenanthrene, terphenyl, and benzonitrile.

which a.o. is dependent on how close E° is to $E^\circ_{\frac{1}{2}}$ for chlorobenzene, is of the order expected for an electron exchange in solution, and for chlorobenzene the measured rate constant k may well be close to k_2 .

When X forms an anion less stable than Cl^- or the reduction potential of BX becomes less negative,¹⁸ the rate of (3) will diminish, and (3) may become the rate determining step, the rate thus being close to $k_3[BX]^{\cdot-}$. $BX^{\cdot-}$ could then be regarded as stable in this context and its approximate concentration deduced from a knowledge of the equilibrium constant of (2), which may be estimated from the difference in half-wave potentials between A and BX.^{17,19} An increase in ΔE of 0.06 V would diminish K with a factor 10 and as $K < 10^{-5}$ in the cases discussed here, $[A]^{\cdot-}$ and $[BX]$ may be regarded as constant; $[A][BX]^{\cdot-}$ would then be diminished nearly 10 times and $[BX]^{\cdot-}$ approximately 10^4 . A similar dependence of k on ΔE would thus be expected regardless of whether (2) or (3) is the rate-controlling step.

On the basis of the available evidence it seems likely that the rate of the electron exchange between $A^{\cdot-}$ and BX is the limiting factor when $BX^{\cdot-}$ decomposes fast, but that the rate of the decomposition of $BX^{\cdot-}$ becomes more significant when X⁻ becomes a poorer leaving group. A quantitative analysis involving more data may illuminate these points.

The rate constant k_4 has been assumed to be high compared to k_7 and k_8 , and (4) thus

contributing to k with a factor $\frac{1}{2}$. This assumption is valid, when the reduction potential of A is much more negative than that of B; if this is not the case, k_7 or k_8 may be larger than k_6 ; k_8 may be larger than k_4 in the indirect reduction of iodobenzene and a number of compounds, where n has been found close to 1; cyclic voltammetric results point in the same direction.^{18, 20-23}

Electron transfer from a tight ion pair to a molecule is slower than from a loose ion pair or a free radical anion.¹⁵ The rate of electron transfer from anthracene to 2-chloropyridine was nearly the same in DMF containing LiCl or tetrabutylammonium iodide; quinoxaline showed a slower exchange in LiCl than in TBAI; this, however, may be due to a complex formation between the base quinoxaline and the Lewis acid Li^+ prior to reduction so an ion pair is formed directly. In tetrahydrofuran an effect may possibly be found of ion pair formation even for aromatic hydrocarbons.

Sometimes the reduction (amalgam formation) of the supporting electrolyte hinders the reduction of a difficultly reducible substrate. It was found that electron transfer from anthracene anion radical to 2-chloropyridine was possible in the presence of Li^+ although the polarographic wave of Li^+ masks the reduction of 2-chloropyridine. This suggests the possibility of reduction of very difficultly reducible BX compounds, provided $\text{BX}^{\cdot-}$ decomposes faster than $\text{R}_2\text{N}^{\cdot-}$.

An anion radical transports only one electron at a time and delivers it to a molecule outside the electrical double layer where the electrode has no influence on the stereochemistry of the product; thus a possible controversy between a one-electron and a two-electron step and a possible stereochemical influence of the electrode may be resolved. The reduction of D,L and meso α, α' -dichlorobenzyl (stilbene dichloride) to stilbene both by means of anion radicals and directly at the electrode suggests two one-electron steps. The cyclopropane formation by reduction of 1,3-dibromides may follow a similar pattern.

The presence of both a proton donor and a BX compound introduces a competition for the anion radical; addition of phenol to a solution containing naphthalene and chlorobenzene results in a decrease of the catalytic wave. A

quantitative treatment of the height of the naphthalene wave in dependence of the concentration of chlorobenzene and phenol would correlate the reaction rates of the anion radical in electron exchange reactions and reactions with proton donors.

EXPERIMENTAL

The polarograph was a Radiometer PO4d Polariter. The N,N -dimethylformamide (DMF) was dried over molecular sieves A4; further drying with Al_2O_3 (Woelm Al_2O_3 W200) directly in the polarographic cell did not change the rate constants found.

A measurement was made as follows: To a solution of tetrabutylammonium iodide in DMF at 25 °C was added the A compound, and the polarogram recorded; an amount of the BX compound was added and the polarogram recorded; more BX was added, a polarogram recorded, and so on until it was apparent from the polarogram that the BX-compound was present in a great excess.

The relative uncertainty of a rate determination is rather large, about 15–30 %, mainly due to the following two facts: When ΔE is small, the waves of A and BX become increasingly difficult to separate at higher concentrations of BX which makes the measurements of the wave-height of A less accurate; when ΔE becomes large, the increase in the wave-height of A is small, and the uncertainty in the relative increase is large.

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